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Tunable degree of oxidation through variation of H_2O_2 concentration and its effect on structural, optical and supercapacitive properties of graphene oxide powders synthesized using improved method

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ABSTRACT

Graphene oxide (GO) powders have been synthesized via improved method (also called Tour's method) by varying concentration of H_2O_2 and the effect of H_2O_2 concentration on its properties has been studied extensively. The synthesized samples were characterized by XRD, TEM, Raman, FTIR and UV–Vis. spectroscopy. The degree of oxidation level in the synthesized samples was estimated from obtained results and the fundamental aspects of correlation between their properties and the degree of oxidation is discussed exclusively. Our results demonstrate that the use of different concentrations of H_2O_2 can control the surface and molecular structures of GO, resulting in the tunable structural, optical and electrochemical properties which could be useful for supercapacitor applications.

1. Introduction

In recent decades, the increasing demand of energy and rising pollution level have pushed researchers to develop new electrode materials as the urgent requirement that enhance the performance and efficiency of supercapacitor for large-scale purposes [1]. Therefore, the synthesis and development of novel carbonaceous materials such as graphene-related materials have become very interesting over recent years. Among various graphene-related materials, graphene oxide (GO) has received enormous interest in supercapacitor applications because of its inexpensive scalable preparation and specific properties [2]. Supercapacitors have become one of the most promising power sources among all the available energy storage devices, because of their high power density, quick charge propagation and durable operational stability compared to the conventional capacitors and batteries [3]. Supercapacitors are mainly of two types based on their charge storage mechanism: electrochemical double layer capacitors composed of carbonaceous materials where ion adsorption occurs at the electrode/electrolyte interface and pseudocapacitors composed of conducting polymers or transition metal oxides involve fast faradaic charge transport reactions [4].

GO is an important derivative of graphene with two dimensional (2D) structures having oxygen containing functional groups such as epoxides and hydroxyl groups located on the basal plane and carbonyl, carboxyl and hydroxyl groups anchored on the edges of the graphene skeleton [5]. The properties of GO arise from the presence of various oxygen containing functional groups is greatly affected by the degree of oxidation. It has been shown that the optical band gap and electrical conductivity in GO can be altered through the control of oxygen containing functional groups [6]. In a recent study, Gao et al. [7] have suggested that the structure of GO with specific oxygen containing functional groups is strongly affected by degree of oxidation which depends on the oxidants used, graphite source and reaction conditions. Starting by Brodie in 1859 [8], several improvements in the formation of GO have been done so far. Among them, Hummers' method [9] is the most common approach to produce GO from the oxidation of graphite. In Hummer's method, some toxic gases are generated during experiment which is the drawback of this method. Recently, Marcano et al. [10] have reported improved method for large scale production of GO without generating toxic gases. In this method, GO is obtained from the oxidation of graphite powder in the mixture of concentrated acid with strong oxidizing agents. The oxygenated graphite powder is then subjected to hydrolysis followed by washing with water and ethanol that gives a colloidal dispersion of GO. Solid GO powder then can be obtained by drying the aqueous dispersion at low temperature. The purpose of low drying temperature is to obtain highly oxygenated GO with variable amount of residual water molecules. It is worthy to note that, in this method, the amount of hydrogen peroxide during experiment plays an important role to control structural and optical behavior of GO. In a report [11], authors have illustrated that the H_2O_2 was added to

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graphite flakes solution until the bright yellow color was achieved. The reported results suggest that the amount of H_2O_2 plays an important role in Tour's method to produce desired quality of GO. However, it is worth to note that till date no one has reported the effect of H_2O_2 concentration on the structural, optical and electrochemical properties of GO synthesized using Tour's method. Hence, one of the major purposes of the present work is to synthesize GO in order to see the effect of different concentrations of H_2O_2 on its structural, optical and electrochemical properties.

In contrast to early attempts on healing defects for making highly conductive graphene, the present attention is now to create and enlarge defects into graphene in a controlled manner in order to enhance different properties useful for energy storage and transfer, sensing and catalysis [12]. The chemical functionalization has become one of the most convenient approaches to create defects in π-electron network of graphene [13] for opening up new possibilities for its various applications. One of the functionalized forms of graphene is GO which has attracted enormous interest because of its ability to produce graphene like structure anchored with oxygen containing functional groups.

Moreover, the lower specific capacitance value of graphene due to lower surface area caused by undesirable agglomeration of graphene nanosheets has led to study the possibility of GO as supercapacitor electrode materials in energy storage devices. The oxygen containing functional groups attached to the surface of GO reduces the aggregation thereby increasing surface area [14]. It has been demonstrated that GO has trapped water and the ions within the GO layers. The ions, mainly protons from hydrolysis of oxygen containing functional groups can move with the assistance of water and contribute to enhance the specific capacitance [15]. In another study [16], the authors have reported that the electrochemical phenomena in GO are closely related to the charge distribution on GO due to attached functional groups and the polarization of water molecules that are considered as dipoles. They have illustrated that the oxygenated functional groups produce negatively charged GO surface by generating a positive charge on graphene and negative charges on O atoms due to polarization of GO. The GO with more functional groups can have stronger surface charge which leads to ordering of water near the GO and the ordered/polarized water molecules between the GO layers form a proton-conducting skeleton. This unique structure of GO with positive and negative charge strongly enhances energy storage capacity.

Many such approaches rely on the fact that GO has inherent electroactive behavior, arising from its unique nature of structure [17]. Researchers have dedicated extensive efforts to determine the electrochemical behavior of GO. However, the detailed mechanism and potential of the oxygen functional groups on GO have not been revealed. The large majority of electrochemical research done on graphene materials so far involves solid-state modification of electrodes. The first report of cyclic voltammetry (CV) in colloidal GO solutions was brought by Chen et al. [18]. The aim of their work and also in other beginning studies [19] was only to achieve deposition of a thin layer of reduced GO onto glassy carbon electrode surface as a result of the cycled potential for sensing application. In a recent report, authors [20] have studied the voltammetry of the aqueous colloidal GO solutions itself, arising from the inherent redox activity of oxygen containing functional groups attached to the surface of GO. They have exploited the electroactive nature of aqueous GO dispersion for future use in electrochemical sensing application. To the best of our knowledge however, there is a shortage of reports on direct electrochemical activity of free GO in solution. Other important goal of this work is to explore electrochemical activity of GO when it exists freely in solution, in comparison to earlier study for electrode surface modification. Towards these above mentioned objectives, we have prepared GO powder with different reaction conditions and systematically investigated structural and optical properties of GO with the measurement of electrochemical activity through cyclic voltammetry in colloidal solutions.

Herein, GO has been synthesized via Tour's method with different concentrations of H_2O_2 and its supercapacitive property has been studied intensely. The present synthesis method is advantageous compared to previous Hummer's based methods because it does not produce toxic gases such as NO_2, N_2O_4, and ClO_2. The synthesized samples namely, GO50, GO70 and GO100 for 50, 70 and 100 ml of H_2O_2, respectively were characterized by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FTIR), Raman and UV–Vis. spectroscopy. The degree of oxidation level was estimated from obtained results and the relationship between properties and the degree of oxidation is discussed. Our results demonstrate that the use of different concentration of H_2O_2 can control the amount of oxygen containing functional group in GO, resulting in the tunable structural, optical and electrochemical properties of GO which could be useful for supercapacitor applications.

2. Experimental

2.1. Materials and synthesis

Graphite flakes, sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrogen chloride (HCl) and absolute ethanol were purchased from Merck (India) and used without further purification. The DI water was used for washing purpose throughout the experiment.

GO powder was synthesized using a procedure based on Tour's method [10]. The schematic diagram of the synthesis procedure is shown in Fig. 1. In this method, the oxidation of graphite flakes is done in water free mixture of concentrated H_2SO_4 and H_3PO_4 using $KMnO_4$. First of all, graphite flakes powder (3.0 g) was added to a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 ml) and then $KMnO_4$ (18.0 g) was slowly added to the mixture under vigorous stirring keeping temperature below 30 °C with the help of water bath. Subsequently, the reaction temperature was fixed to 60 °C and stirred for 12 h. The obtained brown color mixture after successful reaction was cooled to room temperature and poured onto ice of 400 ml DI water. Then, a fixed amount (50, 70 and 100 ml) of 30% H_2O_2 solution was added to the prepared solution in order to make GO with different concentrations of H_2O_2. The reaction mixture was centrifuged at 4000 rpm for 30 min, and the supernatant was decanted. The remaining solid material was washed three times with DI water, absolute ethanol and 5% HCl solution in sequence to remove unreacted materials. The remaining material was further repeatedly washed with DI water to remove the residual salts and acids. Thereafter, the obtained slurry of GO was dried overnight at room temperature in order to get GO powder. The prepared GO powder using 50, 70 and 100 ml of 30% H_2O_2 solution was marked as GO50, GO70 and GO100, respectively.

2.2. The role of H_2O_2 in exfoliation mechanism

It has been observed that the addition of the different concentrations of H_2O_2 changes the colour of mixed solution of graphite flakes from purple to dark brown followed by bright yellow. The colour changes of the mixed solution after adding different concentrations of H_2O_2 confirm that the solution is becoming basic in nature. It is reported that GO can be more exfoliated in basic solution [21]. The obtained results in the present study verify that GO gets more exfoliated as the concentration of H_2O_2 is increased. The role of H_2O_2 in the exfoliation process of graphite sheets could be revealed on the basis of published work [22,23]. The exfoliation mechanism of GO layers using H_2O_2 could be understood through the following processes:

(a) When H_2O_2 is added to the mixed solution, the KOH is formed.
(b) The OH− ions present in the aqueous solution of KOH react with H_2O_2 and forms O_2^{2-} ions.
(c) The O_2^{2-} ions can intercalate into graphite layers and exfoliate it to the graphene layers.